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The Processing of a Novel Polymer Matrix for Wind Turbine Blades

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Abstract

The curing behaviour of a novel composite matrix formulation based on bisphenol A epoxy resin, an anhydride curing agent, and a tertiary amine accelerator is investigated. The curing kinetics are studied using both isothermal and dynamic differential scanning calorimetry (DSC) experiments. The cure kinetics of the thermoset resin are best described by a modified autocatalytic model, where good agreement between experimental and predicted model results is obtained during the initial stages of the cure reaction.

Introduction

This anhydride-cured epoxy resin has been developed by Hitachi Chemical Company Ltd. (HCCL) as a matrix for fibre reinforced wind turbine blades. From initial testing, this resin has shown improved interlaminar and interfacial properties in GFRP laminates, when compared with an existing commercial amine-cured resin system, used in this application [1].

The processing of thermosetting resins is complicated. The mechanism and kinetics of the cure reaction influence the resulting network morphology and, thus, dictate the physical and mechanical properties of both the cured resin and the composite part. Understanding the cure kinetics is critical to control the cure and processing schedules in order to optimise the properties of the final product.

Much work has been conducted to determine appropriate models that describe the cure kinetics of a range of thermoset resins. The simplest models are based on n^{th} order kinetics [2,3]. However, for epoxy resin systems the most widely used model is the autocatalytic model [3,4].

The objective of this study was to model the cure kinetics of this novel matrix with the aim of optimising the processing conditions and cure cycle of the resin. From previous isothermal DSC and rheological studies, it is observed that the cure cycle (12 hours at 75 °C) is inefficient as the maximum degree of cure, α, (86%) is reached after 6 hours [1]. The resin has been developed for application to wind turbine blades and therefore the intended manufacturing route will be vacuum assisted resin infusion. In the manufacture of such a large structure the curing time is critical and very costly.

The potential to optimise the cure opens up the possibility of increasing turnover of parts; significantly reducing the manufacturing cost and at the very least produce better quality parts with uniform cure profile through thickness.

Experimental

Materials

The resin is a blend of three constituents mixed in a specified ratio: bisphenol A diglycidyl ether (DGEBA), methyltetrahydrophthalic anhydride (MTHPA), and Ancamine K54, a blend of tris-2,4,6-(dimethylaminomethyl)phenol (90-95 wt%) and bis(dimethylaminomethyl)phenol (5-10 wt%). The chemicals were supplied by HCCL. The tertiary amine and anhydride are premixed before the addition of the epoxy, the mixture is stirred until homogenised. The mix ratios are propriety to HCCL and hence not reported here.

Differential Scanning Calorimetry

Both dynamic and isothermal DSC experiments were conducted using a TA Instrument Q2000 DSC, under nitrogen at a flow rate of 50 mL/min. Uncured resin samples (6-15 mg) were enclosed in hermetically sealed aluminium pans.

Initially, dynamic scans were conducted, the uncured resin was heated at 10 K/min from 25 °C to 250 °C. The sample was then rescanned under the same conditions, to determine the ultimate glass transition temperature (T_g). Isothermal scans were conducted at four different temperatures ranging from 100-120 °C for 100 minutes.

Rheology

A TA discovery rheometer was used in oscillatory mode (25 mm parallel plates). Isothermal oscillation-time experiments were conducted at the temperatures used in the kinetic study: frequency 1 Hz, normal force 0.1 N and strain 1.5%.

Results and Discussion

The total heat of reaction, H_T, representing the area enclosed by the thermogram, was obtained from several dynamic DSC scans (taken at different ramp rates), Eq. 1. For dynamic scans, using an iterative baseline has been shown in literature to be the most appropriate to be able to capture the effect that heat capacity changes as the resin cures [5]. The average H_T was determined to be 340 J g^{-1}.

$$H_t = \int_{t_1}^{t_2} \frac{H}{dt}\, dt \qquad [\text{J g}^{-1}] \tag{1}$$

Kinetics modelling

The approach taken to study the cure kinetics is to fit the reaction rate profiles, which are obtained from the isothermal and dynamic DSC experiments, to models. As observed in literature for other epoxy/anhydride resins, an autocatalytic model is chosen, Eq. 2 [2].

$$\dot{\alpha} = (k_1 + k_2\alpha^m)(1-\alpha)^n \quad (2)$$

where, $\dot{\alpha}$ is the cure reaction rate, m and n are reaction orders and k_1 and k_2 are reaction rates. In the model by Ryan and Dutta, k_1 is taken to be the initial reaction rate when time (t) and $\alpha = 0$, hence k_2 can be determined using Eq. 3.

$$k_2 = \frac{(2-m)k_1\alpha_p^{1-m}}{m-2\alpha_p} \quad (3)$$

where, α_p is the degree of cure at the maximum rate of reaction.

By using a reduced gradient non-linear optimisation method implemented in Microsoft Excel the model can be fitted to the isothermal runs and the optimum values of m and n values are evaluated.

This original cure model presented a poor fit to the experimental data. Therefore, the equation was modified to Eq. 4 [5], enabling the final stages of the cure to be captured more accurately.

$$\dot{\alpha} = k_1(1-\alpha)^{n_1} + k_2\alpha^m(1-\alpha)^{n_2} \quad (4)$$

The reaction orders; m, n_1 and n_2, were determined using the optimisation solver as had been done previously, Table 1. The model, as shown in Figure 1, fits the initial stages of cure yet at the latter stages (when degree of cure exceeds 65%) the model seems to deviate from the experimental data.

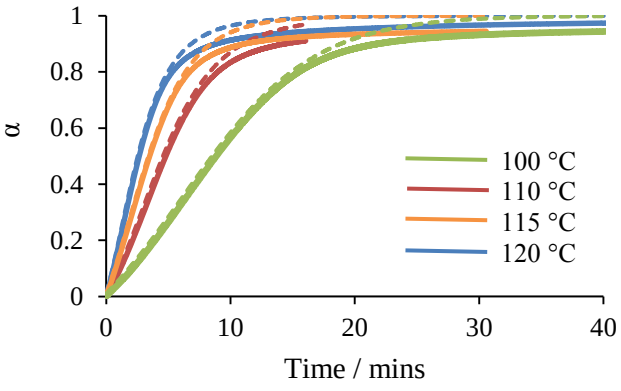

Figure 1: *a) Plot of degree of cure versus time. N.B. dashed line represent the model data and solid line the experimental data.*

This is due to the onset of gelation and vitrification, which reduces the mobility of the reactive groups and therefore the reaction is controlled by diffusion rather than kinetic factors.

Other models are available and are described in literature which allow for this diffusion control to be captured [7]. However, as this model is needed to aid understanding of processing prior to gelation, the current model is sufficient and captures the critical initial cure kinetics well.

T / °C	k_1 s^{-1}	k_2 s^{-1}	m	n_1	n_2
100	0.00074	0.00238	1.015	0.893	1.006
110	0.00125	0.00535	0.951	1.128	1.173
115	0.00200	0.00551	0.980	0.940	1.180
120	0.00263	0.00770	0.905	1.143	1.233

Table 1: *Kinetic model parameters.*

The rate constants increased with temperature following the Arrhenius relationship (Eq. 5). From the linear least-squares fit of ln k_i *versus* 1/T, Figure 2, the pre-exponential factors (A_i) and activation energies (E_{ai}) were determined, Table 2.

$$k_i = A_i e^{\left(\frac{-E_{a_i}}{RT}\right)} \quad (5)$$

Activation energy	
E_{a1} (kJ mol^{-1})	78.5
E_{a2} (kJ mol^{-1})	69.2
Pre-exponential factor	
A_1 (s^{-1})	$e^{18.1}$
A_2 (s^{-1})	$e^{16.3}$

Table 2: *Kinetic parameters E_a and A.*

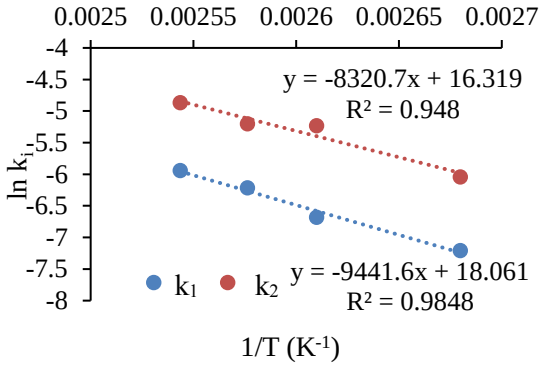

Figure 2: *Linear least-squares fit of ln k_i versus 1/T.*

Kinetics based on isothermal data can only be obtained over a narrow temperature range during the onset of the exothermic peak observed during a dynamic DSC thermogram. To allow informed processing, understanding the cure kinetics over a much wider temperature range is critical, especially in this case where the cure temperature is not within the isothermal scan range. Figure 3, shows the modified model fitted to the dynamic cure of the resin using the kinetic parameters determined from the isothermal study, given in Tables 1 & 2. To determine value of the reaction orders the equations for each varying

with temperature were determined with least squares linear regression. Although there is some discrepancy between the model and experimental data, as the mean squared error is very small 0.003, it is assumed that this is an appropriate model. To improve this fit, better understanding of how the reaction orders vary with temperature is required.

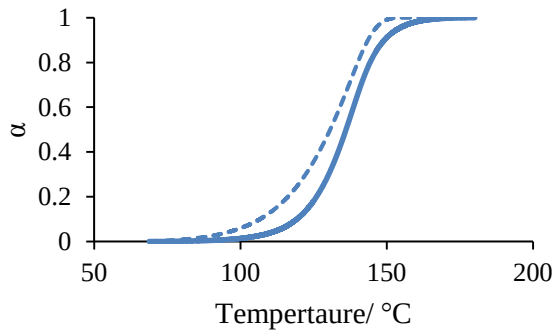

Figure 3: *Plot of degree of cure versus temperature. N.B. dashed line represent the model data and solid line the experimental data*

Gel point determination

The rheological behaviour of the resin at these isothermal temperatures has also been assessed to determine the gel point (a_g) at each temperature. The a_g is critical to the processing of the resin as beyond this point the resin no longer flows, thus closing the available processing window. In this work the a_g was taken to be the crossover point of the storage and loss modulus [8]. Combining the rheological data with the isothermal DSC data, the average α at the a_g for the isothermal experiments was determined to be 30%.

Conclusion

The work undertaken here has allowed the cure kinetics of this novel thermosetting resin to be fitted to a modified autocatalytic model.

The next phase of work is to investigate the effect of different anhydride curing agents upon the cure reaction and hence cure kinetics. The overall aim is to determine which resin system offers the best thermomechanical properties whilst having good interfacial properties with either glass or carbon fibre. The cure cycle for the current blend with MTHPA curing agent is stated to be 12 hours at 75 °C. This is due to manufacture of large components with variable thickness with manufactures choosing long low temperature cycles, to minimise issues associated with thermal gradients through thick composite sections [6]. By understanding the cure kinetics and rheological behaviour of the resin systems, the cure cycle and processing conditions can be optimised to allow for improved quality of manufactured parts with increased production rates.

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